A Method for the Determination of Hypochlorites in Waters

by Harold K. Shaw

May 15th, 1912

Submitted to the School of Engineering of the University of Kansas in partial fulfillment of the requirements for the Degree of Master of Science

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OUTLINE

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A TEST FOR HYPOCHLORITES IN WATER

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In recent years, it has been a question as to whether the addition of calcium hypochlorite to a water as a purifying agent was permissible. The principal ground for the objection was the taste of the residual chlorine or hypochlorite. This is especially noticeable where the hypochlorite is not added carefully and systematically. It will be noticed that at times the Lawrence City water assumes this "hospital" taste indicating an excess of hypochlorite.

In testing for this hypochlorite or free chlorine, it has been customary to use the starch iodide test in acid solution. This gave tests for hypochlorites in most treated waters. About this time it was noticed that many natural waters gave tests for hypochlorite. This could be due to one of two causes. Either some substance in the water might have oxidized the chlorides to free chlorine or else some other substance in the water was giving the test. Taking the first case as impossible because the organic material in water would tend to reduce the oxides of chlorine to chlorides, the second cause will be considered.

In looking for this substance, we will first consider the nature of the common test for hypochlorites. It consists in the liberation of iodine from potassium iodide by the action of the hypochlorite ion in acid solution.

$$Ca^{++} + 2ClO^{-} + 2K^{+} + 2I^{--} + 2H^{+} + SO_4^{--} =$$
$$I_2 + Ca^{++} + 2K^{+} + 2Cl^{-} + SO_4^{--} + H_2O$$

As will be seen, this is purely an oxidation reaction and could be brought about by other oxidizing agents in solution. The two oxidizing agents ordinarily found in natural waters are nitrates and nitrites. With this in mind, I tested several waters for nitrates, nitrites and hypochlorite.

The test used for nitrites was the modified Greiss method. The reagents used are sulfanilic acid and alpha-amidonapthalene acetate. The first is prepared by dissolving 0.5 gm. of sulfanilic acid in 150 cc of acetic acid. The second is prepared by boiling 0.1 gm. alpha-amidonapthalene in 20 cc. of nitrite free water. This solution is filtered through a cotton plug which had been washed with nitrite free water, and 180 cc. of acetic acid added. For use, 2 cc. of each of the above reagents are added to 25 cc. of the water to be tested in a 50 cc. nessler tube. The resulting pink

color is compared with that of the color standards prepared as below.

Permanent color standards for the nitrite determination were prepared as follows: I dissolved 0.2 gm. Fuchsine-S in 50 cc. of 2N HCl and diluted the solution to 2000 cc. with distilled water. I then took 100 cc. of this solution, added 50 cc. of 2N HCl, and made it up to 2000 cc. From this standards were made as follows, each being diluted up to 200 cc.

No.	cc. solution	cc. 2N HCl	Equivalent Nitrite Nitrogen pts.mill.
1	1.5	5.0	.05
2	2.4	5.0	.10
3	3.9	5.0	.20
4	5.5	5.0	.30
5	7.1	5.0	.40
6	8.5	5.0	.50
7	12.6	5.0	.75
8	16.5	5.0	1.00

In order to check up these standards, I prepared a set of standards from a solution of sodium nitrite. Pure sodium nitrite is made from the commercial salt as follows: A hot concentrated solution of silver nitrate was added to a concentrated solution of the sodium nitrite, filtered while hot and allowed to cool. Silver nitrite separates out in fine needle-like crystals which were

filtered off. Hot water was then poured through the filter and the silver nitrite crystallized out as before. These crystals are again filtered off and dried by pressing between sheets of filter paper. I weighed out 0.275 gm. of this pure silver nitrite and dissolved it in hot water and transferred it to a 250 cc. flask. Pure sodium chloride was added till a precipitate ceases to form. The solution is then made up to 250 cc. I diluted 100 cc. of this solution up to 1000 cc. and diluted 10 cc. of this to 1000 cc. Each cubic centimeter of this last is equivalent to 0.0000001 gm. Nitrogen. Taking proportionate amounts of this solution, I made up solutions having amounts of nitrite corresponding to the eight Fuchsine-S standards.

No.	Fuchsine-S	Nitrite
1	.05	.05
2	.10	.09
3	.20	.22
4	.30	.30
5	.40	.41
6	.50	.52
7	.75	.72
8	1.00	.95

These figures are not absolute, but merely an approximation of the shade of color either above or below

the standard. As will be seen, the dye standards conform very closely to those obtained from the nitrite solutions.

I prepared the standard thiosulfate solution to be used in the starch iodide test by dissolving one gram of sodium thiosulfate in a liter of water. To standardize this, I resublimed some iodine and weighed out 0.6355 gm. transferring it to a 500 cc. flask. I then added two grams of potassium iodide and, when the iodine had dissolved, made the solution up to the mark with nitrite free water. The normality of the thiosulfate solution was then obtained by titrating against this iodine solution using starch as an indicator.

DATA

Wt. watch glass ---------	15.3046
Wt. watch glass + I₂ ----	15.9400
Wt. I₂ in 500 cc. -------	.6354

Solution is N/10

	I	II	III
Burette reading No.1	.06	10.11	19.40
" " No.2	8.02	19.40	29.60
c.c. I₂	7.96	9.29	10.20
Burette reading No.1	.10	24.64	.20
" " No.2	20.10	47.20	25.10
c.c. $Na_2S_2O_3$	20.00	22.56	24.90
$\frac{\text{c.c. } Na_2S_2O_3}{\text{c.c. } I_2}$	2.51	2.43	2.44

Average: 2.45c.c. $Na_2S_2O_3$ = 1 c.c. I.

$\frac{0.01}{2.45}$ x .0354 = .000154 gm. Cl per cc. $Na_2S_2O_3$

For the hypochlorite test, I put 100 cc. of the water in a beaker and added 1 cc. of a 10% solution of potassium iodide, 0.5 cc. concentrated sulfuric acid, and 1 cc. of starch solution. After having let the solution stand five minutes, I titrated it with the thio-sulfate solution till the color dissappeared. I found that even distilled water would give a slight blue tinge due to the absorption of nitrites and oxygen from the air. In order to remedy this, I used 200 cc. glass stoppered bottles instead of beakers. As will be seen from the data, all the waters that contained nitrites gave this starch iodide test. The preliminary determinations on known solutions of nitrates did not give the blue color and so the determination of nitrates on the samples of water was dropped.

DATA

No. City Mar. 9	Nitrite	Burette Readings	cc. $Na_2S_2O_3$ used	Calculated: NO_2
4355	.35	10.68-10.90	.22	.41
4355	.10	12.12-12.19	.07	.13
4354	none		none	
4353	.37	13.32-13.73	.21	.40
4857	none		none	
4868	.10	30.71-33.42	2.71	5.1
4882	none		none	
4884	none		none	

I could get a blue color in most any of the waters, even distilled water, if I let it stand long enough. This was due to the absorption of nitrites and oxygen from the air. I tried running a blank on distilled water and titrating it as well as the sample. I found it more satisfactory to not let the solution stand longer than five minutes during which time no blue will be found in the blank. The solution of potassium iodide that I made at the first of the term soon turned yellow, due to the formation of free iodine, according to the equation

$$2KI + CO_2 + H_2O = K_2CO_3 + 2HI$$

$$4HI + O_2 = 2\ I_2 + 2H_2O$$

I tried making up a fresh solution each day and finally just put in two or three crystals of potassium iodide.

As will be seen from the last column, the thiosulfate used to titrate the solution when calculated as nitrite gives values nearly identical to those under "nitrites". This would indicate that the starch iodide test would furnish a good method for determining nitrites. Since this test depends upon the oxidizing power of nitrous acid, the presence of oxidizing agents in the water would make it appear that the nitrites had been increased. On the other hand, reducing agents would cause a decrease. As an example, water No. 4354 re-

quired the addition of some of the iodine solution to give the blue color. This water contained a large amount of albuminoid ammonia.

All this goes to show that the starch iodide test is not a reliable test for hypochlorites, as it will be given in the presence of nitrites. One must look farther to find a test for hypochlorites that will not be interferred with by nitrites.

Mr. Young suggested that I try to get a test with aniline. Aniline when treated with a solution of bleaching powder or with chlorine produces a deep violet color. The reaction probably is:

$$C_6H_5NH_2 + Cl_2 = C_6H_5NHCl + HCl$$

I prepared a bleaching powder solution and standardized it by titrating against the thiosulfate solution. From this, I prepared a solution equivalent to 100 parts per million. I tried shaking some freshly distilled aniline with various amounts of this solution, but got no results either in acid or alkaline solution. This was probably due to the fact that there was no free chlorine in a solution of this dilution.

DATA STANDARDIZATION OF HYPOCHLORITE SOLUTION.

Volume used, 25 cc.	I	II	III
Burette reading No. 1	21.09	23.39	25.67
" " No. 2	23.39	25.67	27.96
Vol. $Na_2S_2O_3$ used -------	2.30	2.28	2.29
and average	2.29		

$$\frac{2.29 \times .000154 \times 1{,}000{,}000}{25} = 14.1 \text{ pts. per million.}$$

$$\frac{100}{14.1} \times 500 = 355$$

355 cc. made up to 500 makes a solution equivalent to 10 parts per million.

Mr. Griffin suggested that a test might be evolved from the fact that the iodine liberated from potassium iodide by a bleaching powder solution could be collected by shaking up the solution with a small amount of chloroform. At first glance this test looked very much like the starch iodide test. Although it is an oxidation reaction, it is not affected by nitrites in neutral or alkaline solution.

In conducting this test, I placed a certain amount, say 2 cc. of the standard bleaching powder solution in a 50 cc., tall form nessler tube. This was then filled up to the mark with distilled water. A crystal of potassium iodide was then added and also a

cubic centimeter of chloroform. The tube was then shaken thoroughly so that the chloroform could become finely divided and come into contact with as much of the solution as possible. It was next allowed to stand and the chloroform settled to the bottom of the tube. It had a pink color due to the dissolved iodine.

I then tried other solvents for iodine. A solvent to be used in this test must be immiscible with water. I tried benzene, carbon bisulfide and kerosene. Benzene and kerosene being lighter than water floated on top and thus were not as desirable as those that remained at the bottom of the solution. Carbon bisulfide seemed better than chloroform, and so was used during the rest of the work. The carbon bisulfide used must be fresh and as pure as can be obtained.

An interesting problem arises at this point concerning the relative solubilities of iodine in carbon bisulfide and in the aqueous solution. Watts' Dictionary says that iodine is four hundred times as soluble in carbon bisulfide than it is in a weake solution of potassium iodide. Therefore, the concentration of iodine in the carbon bisulfide solution is four hundred times that in the water. There are 50 cc. of water

and 1 cc. of CS.

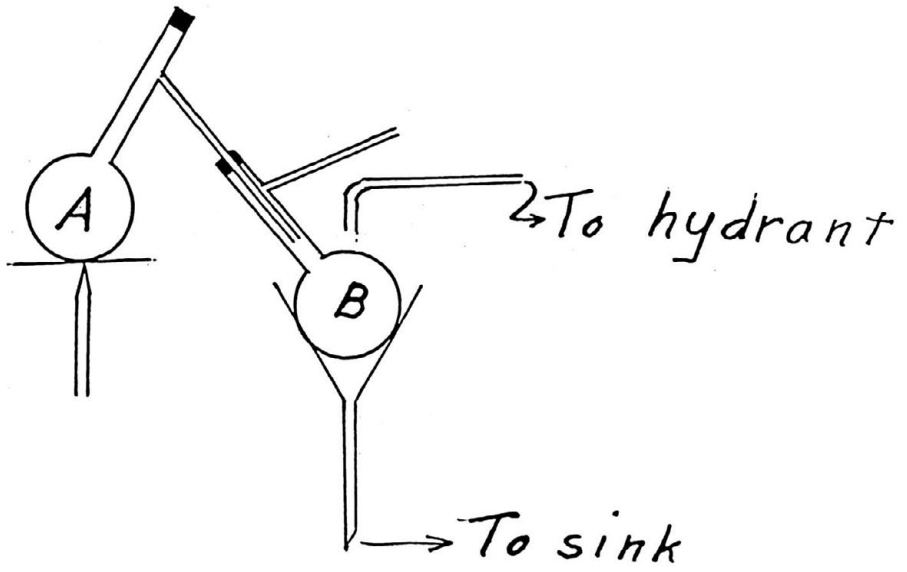
$$\frac{400}{1} \times \frac{1}{50} = \frac{8}{1}$$

Therefore there is eight times as much in the carbon bisulfide as in the water, or one-ninth of the total iodine remains in the water. Thus while we do not get all the iodine each time, we do get eight-ninths of it each time no matter whether we have two or six-tenths parts per million in the solution. In the same manner the carbon bisulfide in the standard has only eight-ninths of the iodine, and the test is just as accurate as if all the iodine was contained in the carbon bisulfide each time.

The problem now resolved itself into the question as to how small a quantity of hypochlorite could be detected by this test. One half cubic centimeter of the solution when made up to 50 cc. was equivalent to one-tenth part per million of available chlorine. Thus, I made up solutions containing one, two, three four and five-tenths parts per million, and applied the test. I got only a very slight tinge of pink with one-tenth part per million, but a good test for two-tenths of a part. I would say, therefore, that the test was applicable for quantities as small as two-tenths parts per million.

I then tried to get results for smaller quantities of hypochlorite by shaking up 1 cc. of carbon bisulfide with 500 cc. of solution in a flask. The particles of carbon bisulfide refused to unite when the settled, and thus no test could be obtained.

I next tried concentrating the solution. In this I used a still composed of two distilling flasks as shown in the diagram.



I placed 400 cc. of a dilute hypochlorite solution in A together with a piece of pumice stone to prevent bumping. The distillate was collected in B. When the liquid had become concentrated to 100 cc., I stopped the distillation, and tested both the residue and distillate. To my surprise, I was not able to de-

test any hypochlorite in either. I tried it again using a larger amount of hypochlorite, but got the same result. The hypochlorite was probably changed over to the chlorate and chloride:

$$3NaClO = NaClO_3 + 2NaCl$$

This reaction is accelerated by the high temperature, and would take place still faster in acid solution.

An interesting study in connection with this was the effect of concentration upon nitrites. I distilled city water, that has considerable amounts of nitrites, in the same manner as I did the hypochlorite solutions. In alkaline solution, no nitrites were found in the distillates, but they were greatly concentrated in the residue. In acid solution, nitrites were found in both distillate and residue and in about the same proportion as in the original water.

DATA

Solution	Original	Distillate	Residue
Alkaline	.8	none	2.5
Acid	.3	.7	.7

I consider my test a quick method of determining how much bleaching powder to add to a water in

order to purify it. With this in mind, I added a known amount of hypochlorite equivalent to five parts per million of free chlorine. I let this stand ten minutes and then tested for the residual hypochlorite.

DATA

Water	Hypochlorite Added	Residual	Consumed
City	.5	.4	.1
4353	.5	.3	.2
4354	.5	.2	.3
4355	.5	.3	.2
4857	.5	.3	.2
4868	.5	.3	.2
4882	.5	.5	.0
4884	.5	.4	.1

In this as well as the rest of my work, I have calculated the hypochlorite as available chlorine because the value of bleaching powder is estimated as so many per cent of available chlorine. My test is accurate enough for this kind of work because one or two-tenths part per million of chlorine in a water does not effect taste.

One trouble about this hypochlorite test is that color standards have to be made up every time the test is used, because the pink color of the iodine soon

fades out of the carbon bisulfide. If permanent color standards are to be made, they will have to be made from a solution of some dye. The fuchsin-S solution used for the nitrite standards matches very closely the pink of the iodine. The only difference is that the dye solution is much more clear than that of the iodine in carbon bisulfide obtained by this method.

The essential part of my test for hypochlorite is that the solution be neutral or alkaline toward litmus. Most natural waters are alkaline, due to the presence of carbonates or bicarbonates. If for any cause the water is acid, it must be made alkaline by the addition of a few cubic centimeters of a sodium carbonate solution, before making a hypochlorite test. No doubt the reader will wonder why the starch iodide test would not do just as well as this if used in alkaline or neutral solutions. I tried this but found that while nitrites did not give the test, the blue color did not appear for quantities less than four parts per million of available chlorine. The shaking out of the iodine in carbon bisulfide is therefore the more delicate.